

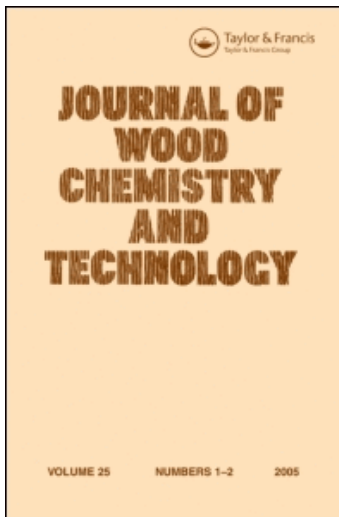
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Lawrence L. Landucci^a

^a U.S. Department of Agriculture, Forest Products Laboratory, Forest Service, Madison, Wis.

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FORMATION OF CARBON-LINKED ANTHRONE-LIGNIN AND
ANTHRAHYDROQUINONE-LIGNIN ADDUCTS

Lawrence L. Landucci, Forest Products Laboratory,
Forest Service, U.S. Department of Agriculture,
Madison, Wis. 53705

KEYWORDS

Anthraquinone pulping, Anthrahydroquinone, Anthrone adduct, Redox catalysts, Delignification, Soda pulping, Lignin, Lignin adducts, ¹³C-labeling.

ABSTRACT

The quinone methide from guaiacylglycol- β -guaiacyl ether [1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol] formed carbon-carbon bonded adducts with both anthrone and anthrahydroquinone (AHQ). It was found that the anthrone adduct [1-(3-methoxy-4-hydroxyphenyl)-1-(anthracen-9-one-10-yl)-2-(2-methoxyphenoxy)ethane] was much more resistant to alkaline degradation than the corresponding AHQ-adduct [1-(3-methoxy-4-hydroxyphenyl)-1-(10-hydroxyanthracen-9-one-10-yl)-2-(2-methoxyphenoxy)ethane]. It was demonstrated by NMR spectroscopy that analogous anthrone and AHQ adducts formed with milled wood lignin and had relative alkaline stabilities consistent with those observed with the model adducts. At 10° C the AHQ-lignin adduct partially decomposed to the γ -monoacetates of coniferyl alcohol and *p*-coumaryl alcohol which subsequently reacted with excess AHQ to give the novel adducts, *trans*-1-(3-methoxy-4-hydroxyphenyl)-3-(10-hydroxyanthracen-9-one-10-yl)propene, and *trans*-1-(4-hydroxyphenyl)-3-(10-hydroxyanthracen-9-one-10-yl) propene, respectively.

INTRODUCTION

In the continuing investigation of the mechanism of redox catalysis of delignification during alkaline pulping,¹ it was of interest to demonstrate the existence of carbon-carbon linkages between the α -carbons of the side chains in the phenyl-propanoid units of lignin and the 10-position of anthrone and 10-hydroxyanthrone (a tautomer of anthrahydroquinone) moieties, as represented by structures Ia and Ib, respectively (Fig. 1). It was expected that these structures would be analogous to the adducts IIa and IIb (Fig. 1), formed by the reaction of a quinone methide (III) of a lignin model with anthrone and anthrahydroquinone.^{2,3}

Transient adduct formation between lignin quinone methides and anthrahydroquinone (AHQ) is thought to be essential to the observed catalytic cleavage of β -aryl ether bonds during alkaline delignification in the presence of AHQ.²⁻⁵ Adduct formation occurs even with simple quinone methides--for example, that arising from vanillyl alcohol.⁶

Considerable evidence has now been assembled to support adduct formation corresponding to structures Ia and Ib, in a milled wood lignin isolated from loblolly pine.

RESULTS AND DISCUSSION

Relative Stabilities of Anthrone- and AHQ-Model Adducts

It has been postulated² that under alkaline conditions both anthrone (in its enolic form) and AHQ add nucleophilically to the α -carbon in the quinone methide III in an analogous fashion (Fig. 2). However, subsequent decomposition of the two resulting adducts cannot follow a common pathway if the mechanism^{2,3} for the previously postulated decomposition of IIb (Fig. 3) is accepted, because of the lack of a hydroxyl group in the 10 position of IIa. Consequently, IIa is likely to be more resistant to alkaline

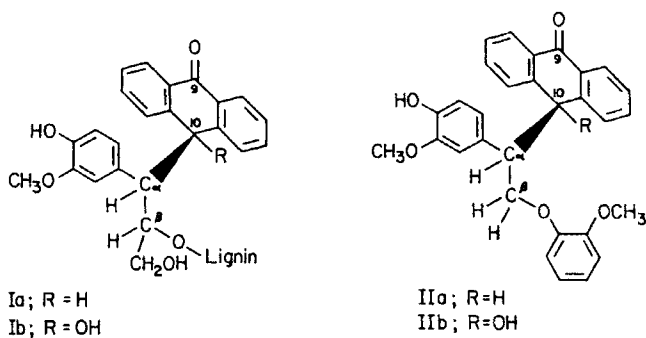


FIGURE 1.--Lignin and model adducts.

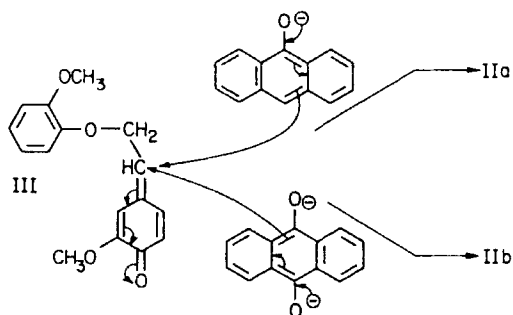


FIGURE 2.--Formation of anthrone- and AHQ-model adducts.

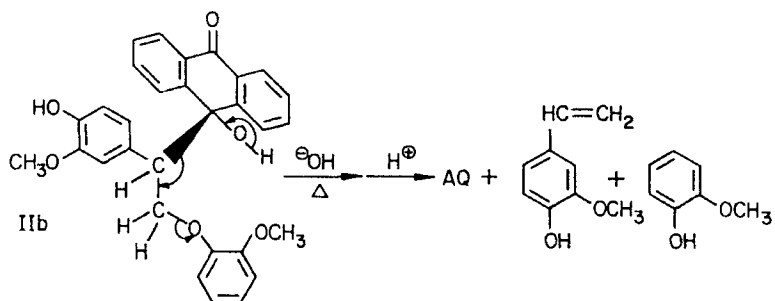


FIGURE 3.--Alkaline degradation of AHQ-model adduct.

degradation. This expectation was confirmed by refluxing the adducts IIa and IIb in alkaline aqueous dioxane in the presence of excess cellobiose, intended to act as a reducing source and to thereby more closely simulate the soda pulping environment. After 1 hr, approximately 70% of IIa was recovered, whereas IIb was quantitatively fragmented into AQ, vinylguaiacol, and guaiacol. Further investigation⁷ revealed that IIa does fragment extensively at 120° C to give guaiacol and a compound (~15%) identified by independent synthesis as IV (Fig. 4), along with starting material (~25%) as the major components in a complex mixture. At 170°, guaiacol and AQ were the major components and no IV was detected. The alkaline degradation pathways of anthrone-model adducts is currently under investigation.

Formation of Lignin Adducts

To form quinone methides in situ in any appreciable rate from free phenolic phenylpropanoid units containing α -hydroxy groups, temperatures of at least 110° C are necessary.⁸ Because much lower temperatures were required to allow adduct formation without subsequent decomposition it was essential to replace the α -hydroxyls in the lignin side chain by better leaving groups. This was accomplished by acetylating the lignin and using a procedure similar to one recently reported for the preparation of IIa.³

Because the carbon-carbon linkage in the model adduct IIa is more resistant to alkaline cleavage than that in IIb, synthesis of the corresponding lignin adduct Ia was first attempted. Treatment of acetylated milled wood lignin with anthrone in alkaline aqueous dioxane at 35° C for several hours gave a mixture which was neutralized and reacylated. Removal of excess anthrone (as anthranol acetate) and a trace of unidentified low molecular weight material from the mixture by gel chromatography left a lignin fraction in 85% yield. The ¹H NMR spectrum of the lignin product (Fig. 5) exhibited a small peak at δ 3.3 which did not exchange with D₂O and is absent in the corresponding spectrum of

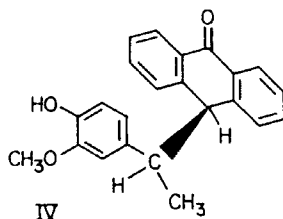


FIGURE 4.--Cleavage fragment from alkaline decomposition of anthrone-model adduct IIa.

the control lignin. This peak is due to intensely shielded methoxyl groups (relative to a normal aromatic methoxyl) which would be expected in a lignin adduct of type Ia on the basis of that observed² in the model adduct IIa (Fig. 5). The high-field methoxyl absorption in the ¹H NMR spectra is a general characteristic of all anthrone and AHQ adducts prepared thus far^{2,3,6} and appears to be relatively insensitive to differences in the side chain of the lignin model. In addition, a small hump appears at $\delta 8.0$ which is likely due to the carbonyl-desielded H-1 and H-8 of the anthrone moiety. The carbonyl signal in the infrared spectrum is a medium absorption at 1670 cm^{-1} , clearly distinct from the strong acetate carbonyl absorption at 1745 cm^{-1} .

When the acetylated lignin was treated analogously with an excess of AHQ at 35°C , the ¹H NMR spectrum was essentially identical with that of the control lignin. Even when the treatment was repeated at 10°C , no high-field methoxyls were observed in the ¹H NMR spectrum. However, gel chromatography of the reaction mixture gave three other low molecular weight products in addition to excess AQ. These were identified as coniferyl acetate, V, and the AHQ adducts VIIa and VIIb (Fig. 6) (all were isolated as their respective diacetates). The formation of all of these products can be easily explained by a sequence of reactions in which V is a primary decomposition product of the AHQ-lignin adduct Ib. Recently, V was also found in the reaction mixture during syn-

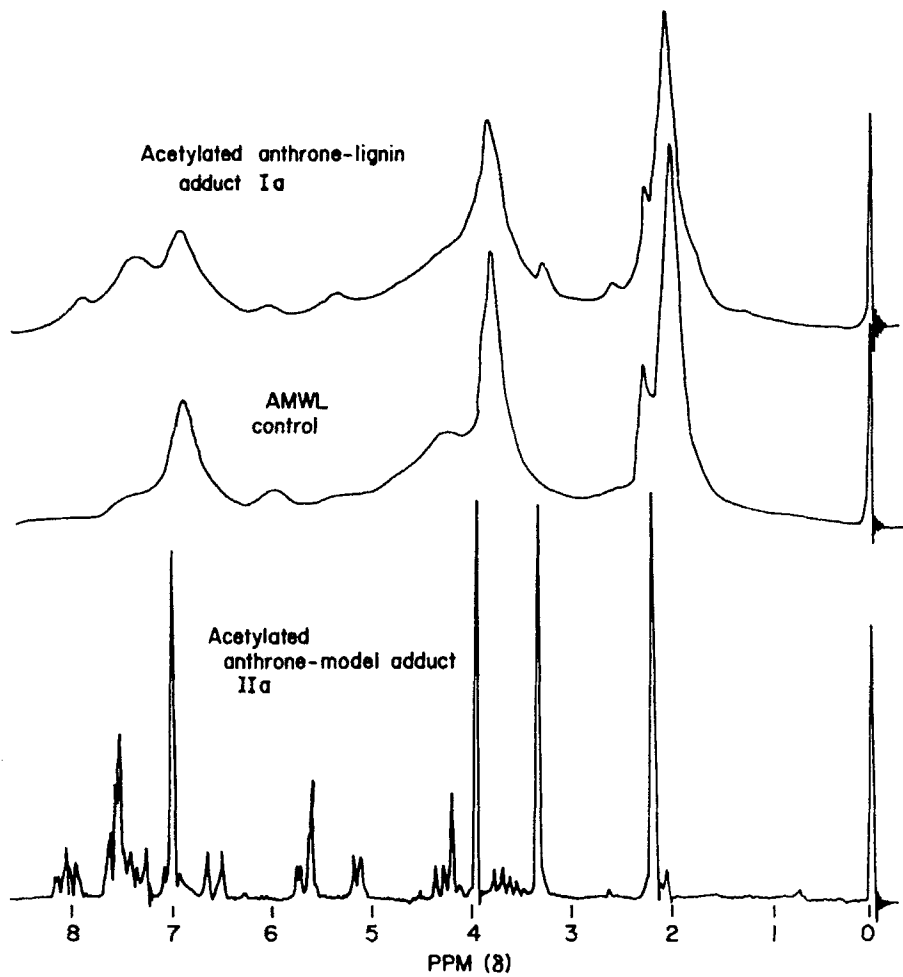


FIGURE 5.-- ^1H NMR spectra of anthrone adducts.

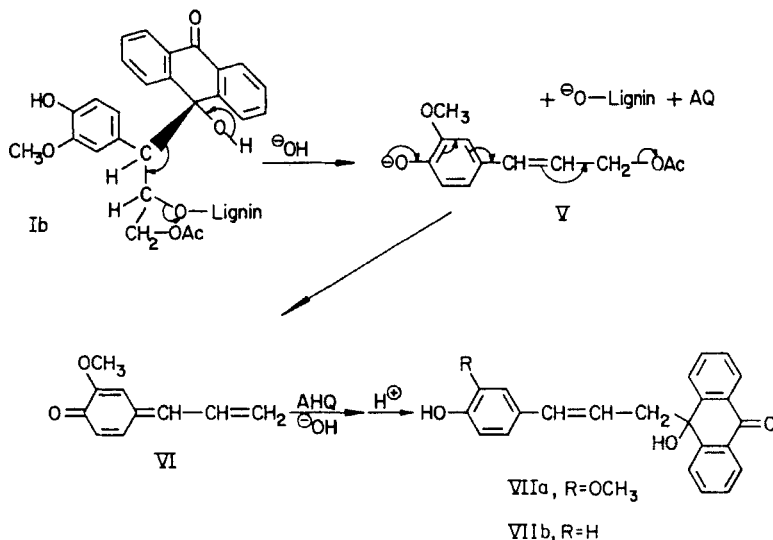


FIGURE 6.--Formation of quinone methide derived from coniferyl acetate and its subsequent reaction with AHQ.

thesis of the model adduct (analogous to **Ib**) derived from guaiacylglycerol- β -guaiacyl ether, and undoubtedly resulted from the partial degradation of the labile adduct.⁹ Under mild conditions, **V** may lose acetate to give the quinone methide **VI**, as the terminal acetate is a good leaving group (at the higher temperatures of typical pulping, the terminal acetate is not essential for quinone methide generation). Subsequent addition of AHQ to the extended quinone methide may then generate the adduct **VIIa**. Because demethoxylation is highly unlikely under the experimental conditions, the adduct **VIIb** must have originated from the corresponding *p*-hydroxyphenyl-glycerol units in lignin. Moreover, under pulping conditions, **VIIa** may dehydrate to give **VIII** (Fig. 7), which may subsequently cyclize, giving the benzanthrone **IX** which has been isolated from spent AQ-soda pulping liquors.^{10,11}

The decomposition products **V** and **VII** indicate that the AHQ-lignin adduct does form, but is relatively unstable in the pres-

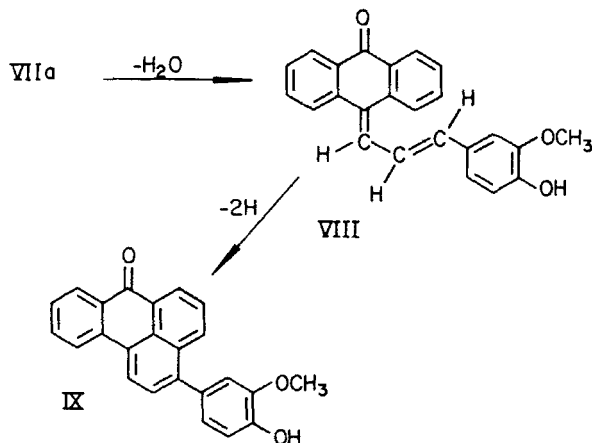


FIGURE 7.--Formation of a benzanthrone derivative.

ence of alkali even at temperatures as low as 10° C, whereas the anthrone-lignin adduct appears to be stable at 35° C. This behavior is consistent with the relative stabilities of the corresponding model adducts IIa and IIb.

Additional evidence of adduct formation in lignin was obtained from the ¹³C NMR spectra (Fig. 8) of the anthrone-lignin adduct formed at 35° C and the AHQ-lignin adduct formed at 10° C using [9,10-¹³C]-anthrone and [9,10-¹³C]-AHQ, respectively. Assignments of C-9 and C-10 absorptions in the ¹³C NMR spectrum of IIa have been made.² Likewise, assignments of the corresponding absorptions in the ¹³C NMR spectrum of IIb have been made^{2,3} and are consistent with those for simpler AHQ adducts.⁶ By superimposing the locations of the ¹³C-9 and ¹³C-10 (heavy arrows, Fig. 8) of the model adducts IIa and IIb on the spectra of the respective lignin adducts it is clear that analogous structures are obtained from lignin. The multiple peaks attributed to the ¹³C-enriched sites in both of the lignin adduct spectra reflect the variety of environments in the lignin macromolecule. The dominance of the ¹³C-10 absorption over the methoxyl peak in the anthrone-lignin

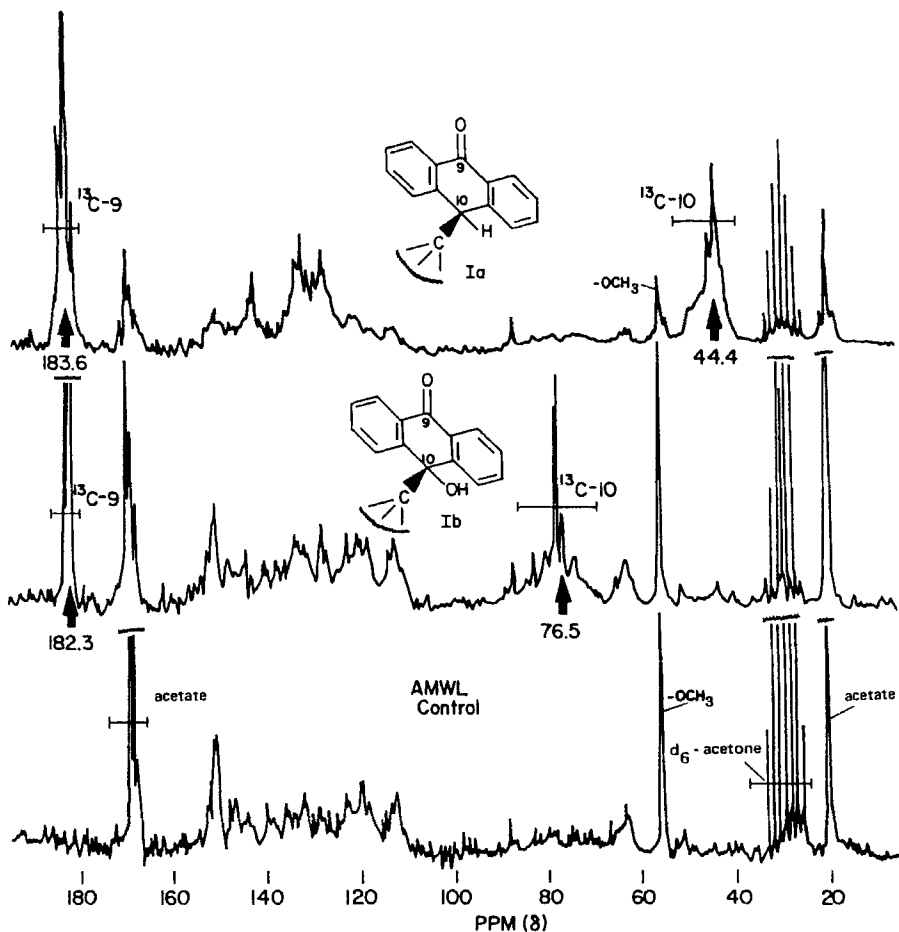


FIGURE 8.-- ^{13}C NMR spectra of anthrone- and anthrahydroquinone-lignin adducts.

adduct spectrum compared to the roughly comparable $^{13}\text{C-10}$ and methoxyl intensities in the spectrum of the AHQ-lignin adduct is indicative of the much lower incorporation of AHQ than anthrone. This is not unexpected considering the relative instability of the AHQ-lignin adduct. Moreover, the lower AHQ incorporation is an explanation for the failure to detect the high-field methoxyl peak

of Ib by ^1H NMR spectroscopy, which is a much less sensitive method than the detection of enriched ^{13}C -10 by ^{13}C NMR spectroscopy.

Upon treatment of the lignin adducts with alkali at 100°C , most of the ^{13}C -9 and ^{13}C -10 absorptions in the ^{13}C NMR spectra of the lignin disappeared and were recovered as ^{13}C -AQ. Those that did not disappear are probably indicative of structure types different from Ia and Ib such as those containing β -carbon linkages rather than the more labile β -ether linkages. Research on the pathways involved in the alkaline degradation of the lignin adducts is continuing.

SUMMARY

It has been demonstrated with NMR spectroscopy that both anthrone (in its enolic form) and anthrahydroquinone react with acetylated milled wood lignin to form adducts linked by carbon-carbon bonds analogous to those previously formed with the lignin model guaiacylglycol- β -guaiacyl ether.

Compounds were isolated and characterized which must have been formed by decomposition of an AHQ-lignin adduct during its preparation at 10°C . Apparently this adduct is extremely labile, whereas the corresponding anthrone-lignin adduct appeared to be much more stable. This observation is consistent with the relative stabilities of the respective model adducts in alkali.

EXPERIMENTAL

Analytical Methods

^1H NMR (60 MHz) spectra of CDCl_3 solutions and ^1H NMR (270 MHz) spectra of d_6 -acetone solutions were determined on a Varian T-60 spectrophotometer and a Bruker WH 270 super-conducting spectrometer, respectively, with tetramethylsilane (TMS) as internal reference. ^{13}C NMR spectra of d_6 -acetone solutions were determined on a JEOL FX 60 (15.00 MHz) spectrometer as totally proton decoupled with TMS as internal reference. Infrared spectra of samples in KBr disks or as films were determined on a Beckman

IR-12 spectrometer. Mass spectra (probe, 80eV) were determined on a Varian MAT 112 spectrometer (Raltech Scientific Services, Inc.).

Starting Materials

Acetylated milled wood lignin (AMWL).--Milled wood lignin prepared by extracting vibratory ball-milled loblolly pine with dioxane/water, 9:1 v/v, was treated with a 1:1 mixture of acetic anhydride/pyridine for 24 hr at room temperature.

9,10-¹³C AQ and 9,10-¹³C anthrone.--The ¹³C-labeled AQ and anthrone were synthesized from phthalic anhydride,¹² prepared quantitatively by cautiously heating phthalic acid (99% ¹³C enrichment in one carboxyl group) in an open flask over a flame until evolution of water ceased.

Synthesis of anthrone-lignin adduct, Ia.--[9,10-¹³C]-Anthrone (0.10 g, 0.52 mmole) was refluxed in 50% aqueous alkaline (0.2M NaOH) dioxane (20 ml) for 5 min under nitrogen. The resulting orange solution was then cooled to 35° C and AMWL (0.20 g) was added. The mixture was then stirred at 35° under nitrogen for 8 hr, the solution was neutralized with acetic acid, and the resulting suspension freeze-dried. The residue was acetylated for 6 hr with 1:1 Ac₂O/pyridine (4 ml) containing a few milligrams of dimethylaminopyridine and followed by a typical workup. A solution of the acetylated mixture in chloroform was applied on a 2.5 x 60 cm column of Bio-Rad Bio-Beads SX-1. Elution with chloroform first removed the anthrone-lignin adduct (0.17 g, 85%) then a low molecular weight unidentified substance (0.010 g, 5%) and finally anthranol acetate (0.077 g, 0.33 mmole, 63% recovery).

Synthesis of AHQ-lignin adduct, IIb.--A mixture of [9,10-¹³C]-AQ (0.17 g, 0.83 mmole), sodium dithionite dihydrate (0.22 g, 1.0 mmole) and 0.5M NaOH (20 ml) was stirred at 30° under nitrogen for 20 min. The dark red solution was neutralized with acetic acid, causing bright yellow AHQ to precipitate. The AHQ was washed with water (10 ml) under nitrogen and dissolved in deaerated dioxane (20 ml). Deaerated water (25 ml) was added and the

resulting suspension cooled to -10° C. The AMWL (0.52 g) in dioxane (10 ml) was added, followed by 1M NaOH (5 ml). The resulting red-brown solution was stirred at $8-12^{\circ}$ C under nitrogen for 16 hr. The mixture, now yellow-brown, was stirred in air for a few minutes, neutralized with acetic acid, and freeze-dried. The residue was acetylated as above, filtered to remove undissolved AQ (0.10 g, 59% recovery) and applied to a gel column. Elution with chloroform removed the AHQ-lignin adduct (0.40 g, 77%), a lignin monomer fraction (0.04 g, 8%), and finally AQ (0.03, 17% recovery) for a total AQ recovery of 76%.

The three major components of the lignin monomer fraction were separated by thick-layer chromatography/on silica gel using 25% ethyl acetate in hexane. Each of the components was isolated as a colorless oil and gave only one spot with TLC.

The first band ($R_f = 0.23$) was identified as the diacetate of VIIa, trans-1-(3-methoxy-4-hydroxyphenyl)-3-(10-hydroxyanthracen-9-one-10-yl) propene (0.014 g, 2.7%); $\nu_{C=O}$ 1766vs, 1688s, $\nu_{C=C}$ 1635s cm^{-1} neat. Mass spectrum m/e (%): 457(M^+ , 2), 398(2), 397(3), 355(5), 354(3), 211(29), 210(55), 206(27), 205(77), 164(17), 163(100), 131(60), 103(15), 43(55). H^1 NMR (270 MHz, d_6 -acetone): δ 2.15 (s, C-10 acetate methyl), 2.16 (s, aromatic acetate methyl), 3.07 [dd (unlabeled at C-10) superimposed on ddd (labeled at C-10), 2 H γ 's, $J_{\gamma\beta} = 7.54$, $J_{\gamma\alpha} = 1.10$, $J_{\gamma-13C-10} = 5.88$], 3.73 (s, methoxyl) 5.44 (dt, H β , $J_{\beta\alpha} = 15.81$, $J_{\beta\gamma} = 7.54$), 5.89 (dd, H α , $J_{\alpha\beta} = 15.81$, $J_{\alpha\gamma} = 1.10$), 6.59 (dd, H-6 in phenyl ring, $J_{6,5} = 8.27$, $J_{6,2} = 1.84$), 6.69 (d, H-2 in phenyl ring, $J_{2,6} = 1.84$), 6.85 (d, H $_5$ in phenyl ring, $J_{5,6} = 8.27$), 7.5-8.2 (m, 8 aromatics in anthracenyl ring); ^{13}C NMR (15.0 MHz, d_6 -acetone): δ 79.2 (C-10), 183.2 (C-9).

The second band ($R_f = 0.33$) was identified as the diacetate of VIIb, trans-1-(4-hydroxyphenyl)-3-(10-hydroxyanthracen-9-10-yl) propene (0.004 g, 0.8%); $\nu_{C=O}$ 1758vs, 1668s, $\nu_{C=C}$ 1634s cm^{-1} neat. Mass spectrum m/e (%): 427 (M^+ , 1), 368(2), 367(4), 325(2), 324(3), 211(24), 210(67), 176(14), 175(65), 134(15), 133(100),

105(11), 43(41). ^1H NMR (270 MHz, d_6 -acetone): δ 2.14 (s, C-10 acetate methyl), 2.21 (s, aromatic acetate methyl), 3.09 [dd (unlabeled at C-10) superimposed on ddd (labeled at C-10), 2 H_Y 's, $J_{Y\beta} = 7.54$, $J_{Y\alpha} = 1.10$, $J_{\alpha-13\text{C-10}} = 5.88$], 5.47 (dt), H_β , $J_{\beta\alpha} = 15.81$, $J_{\beta\gamma} = 7.54$), 5.90, (dd, H_α , $J_{\alpha\beta} = 15.81$, $J_{\alpha\gamma} = 1.10$), 6.93 (dt, H-3 and H-5 in phenyl ring, $J_{3,2} = J_{5,6} = 8.82$, $J_{3,5} = 2.02$), 7.04 (dt, H-2 and H-6 in phenyl ring, $J_{2,3} = J_{6,5} = 8.82$, $J_{2,6} = 2.21$), 7.5-8.2 (m, 8 aromatics in anthracenyl ring).

The third band ($R_f = 0.47$) was identified as the diacetate of coniferyl alcohol (0.012 g, 2.3%); $\nu_{\text{C=O}}$ 1745s, 1770s cm^{-1} neat. Mass spectrum m/e (%): 264 (M^+ , 18), 223(17), 222(100), 214(23), 213(11), 212(37), 163(13), 151(12), 147(10), 131(29), 124(12), 119(14), 103(12), 91(13), 43(76). ^1H NMR (270 MHz, d_6 -acetone): 2.04 (s, aliphatic acetate methyl), 2.33 (s, aromatic acetate methyl), 3.85 (s, methoxyl), 4.70 (dd, 2 H_Y 's, $J_{Y\beta} = 6.25$, $J_{Y\alpha} = 1.47$), 6.37 (dt, H_β , $J_{\beta\alpha} = 15.81$, $J_{\beta\gamma} = 6.25$), 6.69 (dd, H_α , $J_{\alpha\beta} = 15.81$, $J_{\alpha\gamma} = 1.47$), 7.0-7.3 (m, 3 aromatics).

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